



# Effect of Pt:Pd ratio on CO and hydrocarbon oxidation

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## ABSTRACT

For several reasons, typical diesel oxidation catalysts (DOCs) contain a mixture of Pt and Pd and in this study, the effect of the Pt:Pd ratio on a DOC's ability to oxidize CO and different hydrocarbon types was investigated. The concentrations and types of pollutant species were used to simulate those found in low temperature combustion (LTC) engine exhaust. Representative hydrocarbon species were selected; C<sub>2</sub>H<sub>4</sub> (short-chain alkene), C<sub>2</sub>H<sub>6</sub> (short-chain alkane), C<sub>6</sub>H<sub>14</sub> (long-chain alkane) and C<sub>7</sub>H<sub>8</sub> (aromatic). Two types of experiments were performed, one in which the oxidation of each hydrocarbon or CO reactant was examined individually (simple feed conditions), and the second in which all reactants were added together (full feed conditions). Under the simple feed conditions, CO and C<sub>2</sub>H<sub>6</sub> oxidation increased with increasing Pd content, while C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>14</sub> oxidation improved with higher Pt content. When the full mixture of CO and hydrocarbons was used, hydrocarbon oxidation light off consistently followed that of CO, regardless of the Pt:Pd ratio, due to strong inhibition by CO. The best CO oxidation activity was observed over the Pd-only catalyst, and performance over the bimetallic samples was a function of both CO inhibition and Pt:Pd ratio. More specifically, as Pd content increased, CO inhibition was dampened, and as Pt content increased its inherent activity toward alkene oxidation became significant. Since inhibition is a function of the Pt/Pd content and the individual metals have different inherent activities toward the oxidation of different hydrocarbons, results obtained from the experiments with the simple feed could not be directly correlated to those from the experiments with the mixture of hydrocarbons.

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## 1. Introduction

Recently, low temperature combustion (LTC) engines have been developed to meet ever tightening fuel economy standards [1,2]; a challenge from the emissions standpoint is the relatively lower exhaust gas temperature and higher concentrations of CO and hydrocarbons [2–4]. This puts emphasis on the need to design and develop improved low temperature oxidation catalysts for LTC engine exhaust treatment. In evaluating such catalysts, often a single pollutant is used but predicting catalytic activity based on such results may be complicated due to the co-existence of multiple reactant species, their mutual inhibition and inhibition via formation of surface intermediate species [4–6]. For example, Patterson et al. [5] reported that the addition of 1% CO in the feed severely inhibited the oxidation activity of hexane, toluene and benzene over a Pt/Al<sub>2</sub>O<sub>3</sub> monolith catalyst. The authors attributed this to

the competitive adsorption of CO and hydrocarbons onto the catalyst surface. Similarly, Hazlett et al. [4] noted strong CO inhibition of C<sub>3</sub>H<sub>6</sub> oxidation, as well as C<sub>3</sub>H<sub>6</sub> inhibition of CO oxidation. The former was attributed to the strong adsorption of CO on the precious metal sites, and the latter to C<sub>3</sub>H<sub>6</sub> partial oxidation surface intermediates blocking active sites.

The typical oxidation catalyst formulation found in the literature has shifted from a Pt-only precious metal composition to a bimetallic Pt/Pd system. The addition of Pd, when substituted for Pt, of course lowers catalyst cost, but Pd also improves thermal resistance as it has been shown to slow Pt particle sintering [7,8]. And of course it has its own oxidation performance [9,10]. There have been several studies examining the effect of Pt:Pd ratio on CO and hydrocarbon oxidation [11–13]. For example, Skoglundh et al. [11] have shown that for different Pt:Pd ratios, the bimetallic catalysts outperformed the monometallic samples. However, there was not one ratio that proved best for all the species examined; a 1:4 Pt:Pd ratio was best for CO and C<sub>7</sub>H<sub>8</sub> oxidation, and the 1:1 for C<sub>3</sub>H<sub>6</sub> oxidation. Shakya and coworkers [14] studied a variety of Pt:Pd blends and demonstrated that more Pt led to improved C<sub>3</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>, C<sub>10</sub>H<sub>22</sub>

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**Table 1**  
Sample content as a function of Pt:Pd ratio.

Sample	Pt:Pd molar ratio	Content of metal atom ( $\text{mol}/\text{ft}^3 \cdot \text{monolith}$ )		Content of metal mass ( $\text{g}/\text{ft}^3 \cdot \text{monolith}$ )	
		Pt	Pd	Pt	Pd
Pt-only	100:0	$1.42 \times 10^{-1}$	–	27.8	–
3:1 Pt:Pd	75:25	$1.07 \times 10^{-1}$	$0.35 \times 10^{-1}$	20.8	3.8
1:1 Pt:Pd	50:50	$0.71 \times 10^{-1}$	$0.71 \times 10^{-1}$	13.9	7.6
1:3 Pt:Pd	25:75	$0.35 \times 10^{-1}$	$1.07 \times 10^{-1}$	6.9	11.4
Pd-only	0:100	–	$1.42 \times 10^{-1}$	–	15.1

and NO oxidation, whereas CO oxidation was best over the higher Pd content catalysts. Finally, Kim et al. [12] systematically studied Pt:Pd ratio effects and found that better performance for NO and  $\text{C}_3\text{H}_6$  oxidation, when evaluated as a mixture, was found with a Pt-rich bimetallic catalyst. They also showed that the optimal ratio changes with aging and the addition of other gas components.

In this study, we used both simple feed flows (CO or hydrocarbon and  $\text{O}_2$ ) as well as more complex mixtures in order to (i) understand the role of the precious metal ratio on oxidation activity, including inhibition characteristics, and (ii) evaluate the reliability of simplified simulated mixtures in determining the performance under more realistic conditions. The hydrocarbon species selected were a short-chain alkene (ethylene,  $\text{C}_2\text{H}_4$ ), a short-chain alkane (ethane,  $\text{C}_2\text{H}_6$ ), a long-chain alkane (hexane,  $\text{C}_6\text{H}_{14}$ ) and an aromatic (toluene,  $\text{C}_7\text{H}_8$ ) species as representative hydrocarbon molecules. CO and NO were also included in the feed gas.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

A series of five catalyst samples were prepared: 1:0, 3:1, 1:1, 1:3 and 0:1 Pt:Pd supported on an  $\text{Al}_2\text{O}_3$  washcoated cordierite monolith ( $1.59 \text{ g}/\text{in}^3$   $\text{Al}_2\text{O}_3$ , 400 cpsi). The total Pt and Pd metal content was kept constant,  $1.42 \times 10^{-1} \text{ mol}/\text{ft}^3$  of monolith, regardless of the Pt and Pd ratio. All the values are listed in Table 1. The  $\text{Al}_2\text{O}_3$  washcoated monolith was provided by Johnson Matthey. The Pt and Pd precursors,  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  and/or  $\text{Pd}(\text{NO}_3)_2$  (Sigma-Aldrich), were mixed to form aqueous solutions, into which the  $\text{Al}_2\text{O}_3$  washcoat monoliths were dipped. The monolith samples were dried at  $80^\circ\text{C}$  for 24 h and subsequently calcined at  $550^\circ\text{C}$  for 4 h in air. All monolith catalysts were hydrothermally aged in a flowing mixture of 14%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  and  $\text{N}_2$  balance at  $700^\circ\text{C}$  for 24 h.

Pulsed CO chemisorption was used to measure metal dispersion and particle size, with the sample scraped off from the cordierite. The powder was pretreated in 10%  $\text{H}_2/\text{Ar}$  at  $500^\circ\text{C}$  for 1 h, then the temperature was lowered to  $35^\circ\text{C}$  in an Ar flow. CO pulses, ( $1.12 \times 10^{-6} \text{ mol}$ ) were injected until no CO uptake was observed. The metal dispersion and mean particle sizes were calculated using standard dispersion and particle size calculations [15,16], and specific metal surface areas were taken from references [17,18]. A 1:1 adsorption stoichiometry was assumed and for the bimetallic samples, a weighted average for the metals based on ratio was used for density and weight. Identical Pd and Pt interatomic distances were assumed for simplification, and the resulting dispersions and mean particle sizes are summarized in Table 2. Samples with higher Pd content had higher dispersions/smaller particle sizes, attributed to the thermal stability found with Pd addition to Pt under oxidizing conditions [8,19].

### 2.2. Catalytic performance test

A monolith catalyst (3/4" diameter and 2" long) was wrapped in insulation to prevent gas bypass and was placed in a quartz tube

**Table 2**  
Dispersion and particle size.

Sample	Dispersion (%)	Particle size (nm)
Pt-only	5.8	19.4
3:1 Pt:Pd	15.6	7.2
1:1 Pt:Pd	21.7	5.2
1:3 Pt:Pd	23.5	4.8
Pd-only	26.4	4.3

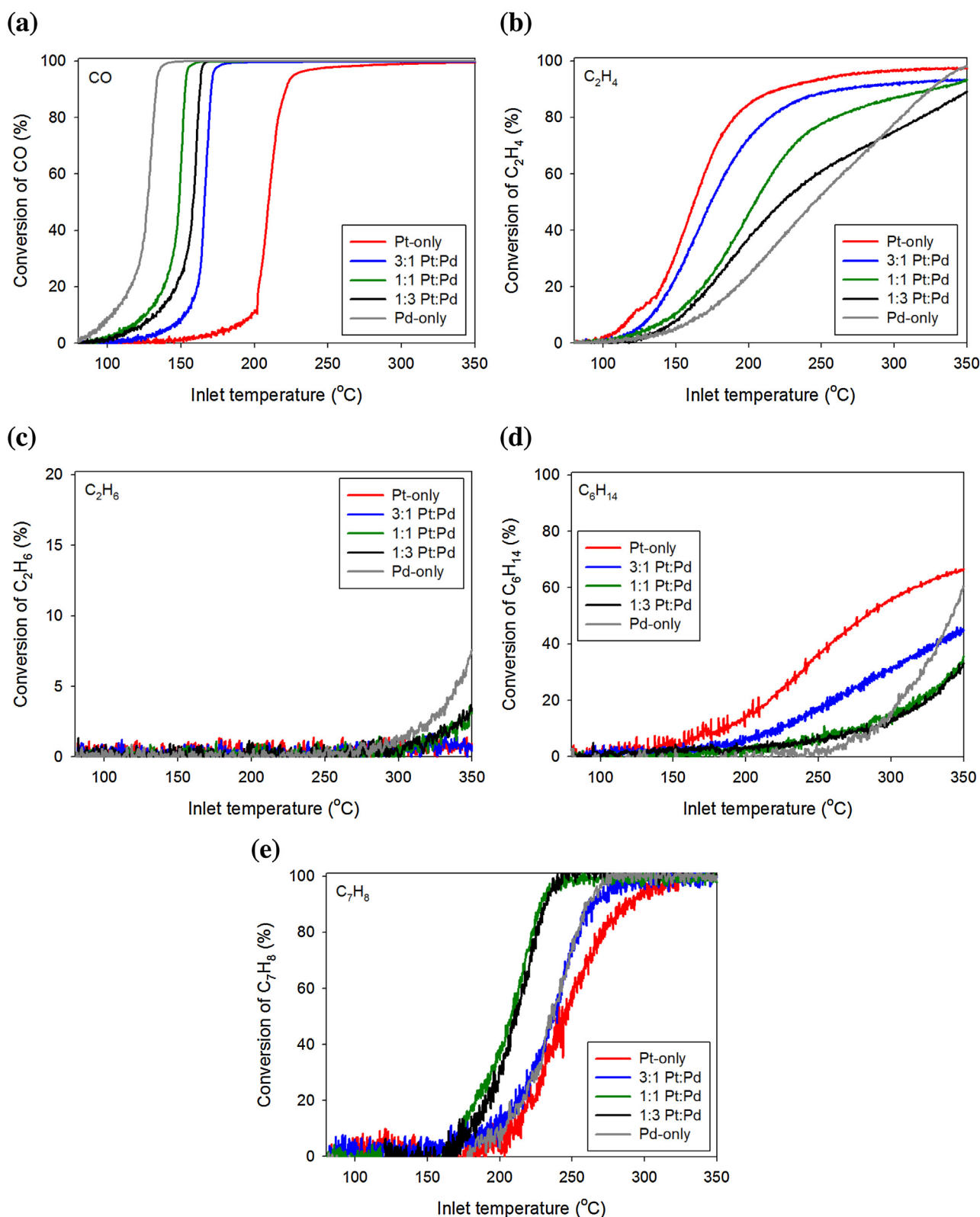
reactor. Four thermocouples were placed in the reactor to measure the gas temperature  $\sim 2 \text{ cm}$  upstream of the catalyst, front and back temperatures of the monolith core, and the reactor wall at the catalyst inlet. The data are plotted versus inlet gas temperature. The gas mixture used for the "complex" feed contained 5500 ppm CO, 150 ppm  $\text{C}_2\text{H}_4$ , 150 ppm  $\text{C}_2\text{H}_6$ , 260 ppm  $\text{C}_6\text{H}_{14}$  and 50 ppm  $\text{C}_7\text{H}_8$ , 30 ppm NO, 10%  $\text{O}_2$ , 5%  $\text{CO}_2$ , and 5%  $\text{H}_2\text{O}$  in a  $\text{N}_2$  balance. Similar experiments, but with respect to a single reactant (CO or hydrocarbon) were also performed to compare the catalytic oxidation activity of the individual components to its oxidation in the more complex mixture. The reactor space velocity of both full mixture and simple feed conditions was  $50,000 \text{ h}^{-1}$ . Water and liquid hydrocarbons,  $\text{C}_6\text{H}_{14}$  and  $\text{C}_7\text{H}_8$ , were vaporized and introduced into the reactor using Bronkhorst CEM liquid delivery systems. The reactor effluent concentrations were monitored using a MKS MultiGas 2030 FTIR analyzer. A pretreatment was used prior to each test, with a feed containing 14%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$  and  $\text{N}_2$  balance at  $600^\circ\text{C}$  for 1 h.

## 3. Results and discussion

### 3.1. Simple feed conditions

Simple feed conditions refer to the experiments where a single pollutant reactant was considered, i.e. CO oxidation, or ethylene oxidation, etc. CO and individual hydrocarbon species oxidation were evaluated as a function of the Pt:Pd ratio. As shown in Fig. 1a, CO oxidation consistently improved with increasing Pd content in the catalyst, ultimately resulting in the best reactivity observed over the monometallic Pd catalyst. This is consistent with previous work that has shown CO oxidation  $T_{50}$  (temperature at which 50% conversion is observed) values monotonically decreased with increasing Pd levels [20]. This is also consistent with Pd being less sensitive to CO self-poisoning compared to Pt [21,22]. Moreover, the addition of the smallest amount of Pd had the most significant impact, with the largest change in  $T_{50}$  occurring between the monometallic Pt sample and the 3:1 Pt:Pd sample. Note, although there was also a significant difference in particle size between the monometallic Pt samples and the bimetallic samples, the overall performance was not solely due to this parameter, as otherwise light off would have been observed at similar temperatures, which was not the case. Conversion was observed at lower temperature with the addition of Pd.

The opposite trend was observed in  $\text{C}_2\text{H}_4$  oxidation as a function of Pt:Pd ratio (Fig. 1b), where a higher relative Pt content led to

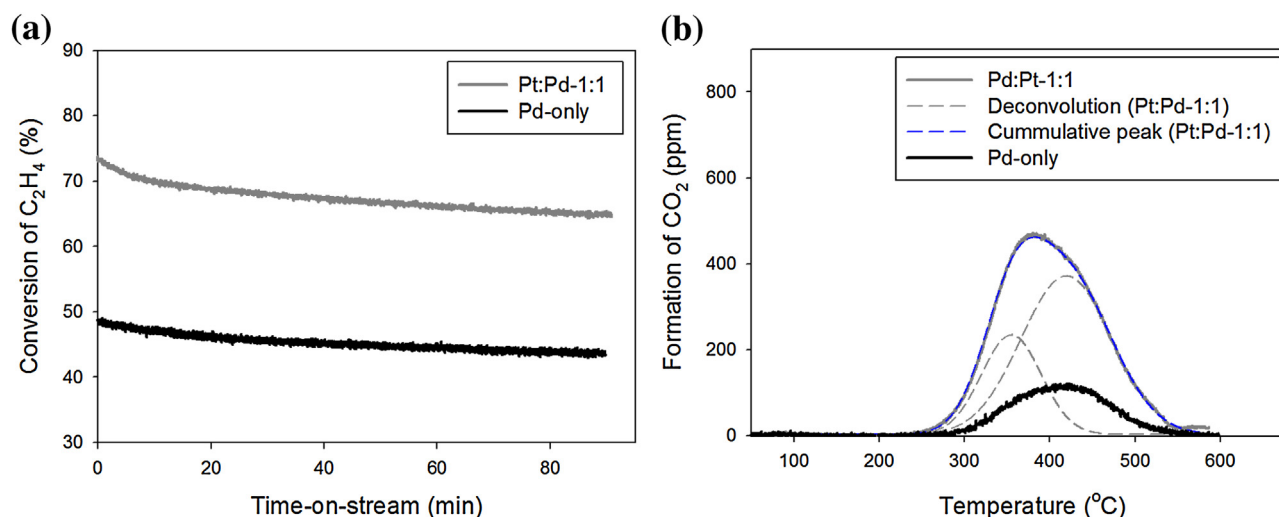


**Fig. 1.** Effect of Pt: Pd ratio on (a) CO, (b) C<sub>2</sub>H<sub>4</sub>, (c) C<sub>2</sub>H<sub>6</sub>, (d) C<sub>6</sub>H<sub>14</sub> and (e) C<sub>7</sub>H<sub>8</sub> oxidation activity under the simpler feed conditions. Feed: 5500 ppm CO or 150 ppm C<sub>2</sub>H<sub>4</sub> or 150 ppm C<sub>2</sub>H<sub>6</sub> or 260 ppm C<sub>6</sub>H<sub>14</sub> or 230 ppm C<sub>7</sub>H<sub>8</sub>, 10% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O and N<sub>2</sub> balance at a space velocity of 50,000 h<sup>-1</sup>.

greater reactivity. This is again consistent with previous literature observations, where Pt was found to be more active in olefin and paraffin oxidation than Pd [5,11,12]. Etheridge et al. [13] reported similar behavior for C<sub>3</sub>H<sub>6</sub> oxidation under lean conditions such

as those used in this work, an increase in the Pt ratio in a Pt-Pd bimetallic catalyst led to better C<sub>3</sub>H<sub>6</sub> oxidation.

A trend also exists in the rate of change in C<sub>2</sub>H<sub>4</sub> conversion (slope of the conversion curve as a function of temperature), which increased with Pt content. As the Pd content increased, the rate's



**Fig. 2.** (a)  $C_2H_4$  oxidation conversion as a function of reaction time, and (b)  $CO_2$  formation during a TPO with ramp rate of  $8^{\circ}C/min$  after the time on stream tests; measured using the Pd-only and 1:1 Pt:Pt catalysts. Feed: (a) 150 ppm  $C_2H_4$ , 10%  $O_2$ , 5%  $H_2O$ , 5%  $CO_2$  and  $N_2$  balance at a space velocity of  $50,000 h^{-1}$ , (b) 10%  $O_2$  and  $N_2$  balance at a space velocity of  $5000 h^{-1}$ .

sensitivity to temperature decreased, especially in the  $250\text{--}300^{\circ}C$  range. This would normally be attributable to activation energy values, as a measure of the reaction's sensitivity to temperature, but the monometallic Pd results point to another possibility. These data suggest a buildup of coke, or some carbonaceous intermediate, on the surface leading to site blocking and therefore reaction inhibition. To test this hypothesis, time on stream experiments with the 1:1 Pt:Pt and the monometallic Pd samples were performed, and example data are shown in Fig. 2a. Ethylene conversion over both catalysts decreased with time, though the Pd sample resulted in less activity loss than that observed with the 1:1 Pt:Pt catalyst. This is seemingly contradictory to the data shown in Fig. 1b, but a lower overall conversion was also achieved explaining the less significant drop. A temperature-programmed oxidation (TPO) characterization was run after each time on stream test, with the  $CO_2$  evolved shown in Fig. 2b. A much smaller amount of  $CO_2$  desorbed from the Pd-only catalyst compared to the 1:1 Pt:Pt catalyst, consistent with the data from Fig. 2a. Such data would suggest that the opposite trend should have been observed, a slower rate of change in conversion with the 1:1 since there was more surface carbon buildup. However, it is apparent there are two TPO features associated with the bimetallic sample. The higher temperature feature is common to both samples, and this we attribute to the buildup of the inhibiting species causing the conversion rate change observed.

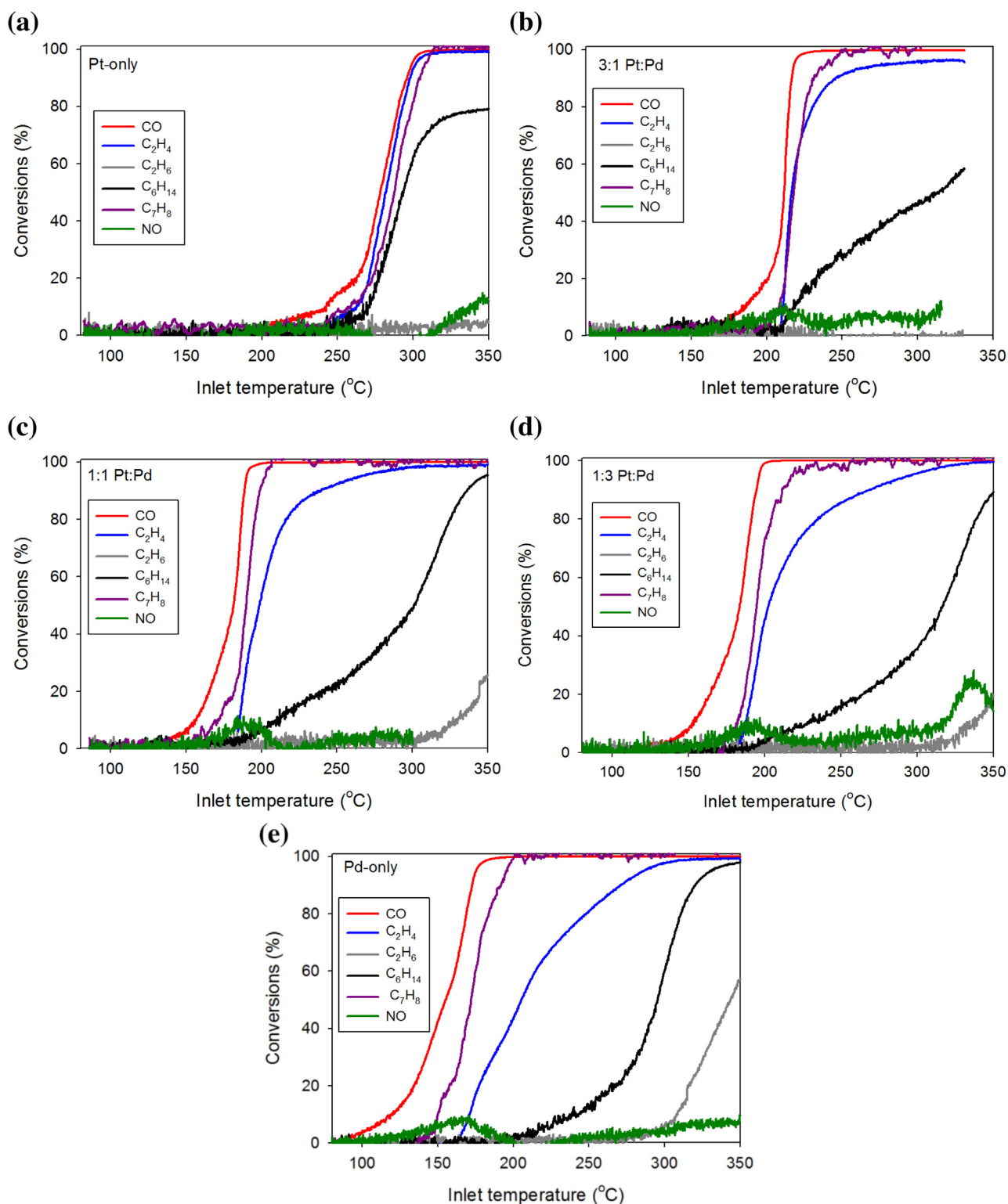
The lower temperature feature is only associated with the bimetallic and its desorption temperature is near that where, although slight, an inflection is observed in the conversion profiles in Fig. 1b (most noticeable with the 1:3 sample). Previous work, but evaluating  $C_3H_6$  oxidation [4], has shown a series of intermediates form on a Pt/ $Al_2O_3$  sample and the  $C_3H_6$  oxidation pathway has been shown to go through a surface ethylene intermediate that inhibits oxidation as does an acetate species which forms during the stepwise oxidation process. Furthermore, CO has been observed as a  $C_3H_6$  partial oxidation product and been considered an intermediate in the route to  $CO_2$  formation [24], and Pd is less prone to inhibition by CO [21,22] as is also noted by the data in Fig. 1a. The inflection noted at  $125\text{--}130^{\circ}C$  for the monometallic Pt sample is indeed likely due to intermediate CO formation. Therefore, the lower temperature feature we assign to a separate intermediate species that forms in the presence of Pt and induces the plateauing in conversion observed at high temperatures, such that ultimately the monometallic Pd sample can achieve higher conver-

sions although had the higher light off temperature. This lack of impact on the monometallic Pd sample may be related to the Pd existing primarily as the oxide, whereas in bimetallic systems, the Pt has been shown to facilitate Pd reduction such that some portion exists in the metal state [7]. This is supported by the findings of Persson et al. [23] who reported that on a monometallic Pd catalyst the Pd existed primarily as Pd oxide, while oxide formation was negligible on the Pt-rich bimetallic catalyst.

In the case of  $C_2H_6$  oxidation, although not so obvious because of the small conversions attained, the trend as a function of Pt:Pt ratio was opposite to that of the  $C_2H_4$ . With increasing Pd content, more conversion was observed, as shown in Fig. 1c. Little overall conversion was attained due to the relative stability of the  $C_2H_6$  molecule. This trend in activity behavior is consistent with  $CH_4$  oxidation, where Pd is considered more active than Pt [25,26]. Note, in a separate experiment the possibility of ethane steam reforming was examined with the monometallic Pt and Pd catalysts. Indeed reforming was observed on the monometallic Pd catalyst starting at  $250^{\circ}C$ , while none was observed with the Pt sample up to  $350^{\circ}C$ . Therefore, the ethane conversion noted is not through oxidation with  $O_2$ , but through steam reforming.

In terms of the longer chain alkane, catalytic  $C_6H_{14}$  oxidation as a function of Pt:Pt ratio (Fig. 1d), followed a similar trend as  $C_2H_4$  oxidation. More Pt led to better oxidation performance, particularly in the temperature region below  $300^{\circ}C$ . Higher temperatures were not used to evaluate performance in order to avoid the homogeneous oxidation chemistry that was observed above  $350^{\circ}C$ . In comparing the trends in alkane species, it is apparent that reactivity as a function of the Pt:Pt ratio strongly depends on the chain length, as has been previously reported [27,28]. Pd performs better in oxidizing the shorter chain length alkanes, and Pt the longer. A possible explanation for this difference in trend when comparing  $C_6H_{14}$  and  $C_2H_6$  may be the different efficiencies Pt and Pd have in activating hydrocarbon C–H versus C–C bond cleavage. Pt metal is more active in breaking C–C bonds, while Pd oxide is for C–H bonds [23,29]. With the longer chain and therefore larger prevalence of C–C bonds,  $C_6H_{14}$  oxidizes more readily over the Pt surface, while  $C_2H_6$  does over the Pd surface. An anomalous trend at high temperature was observed with Pd, similar to what was observed in  $C_2H_4$  oxidation. Again, this is attributed to monometallic Pd being less prone to inhibition by partial oxidation surface intermediates.





**Fig. 3.** Oxidation performance demonstrated by conversion for the (a) monometallic Pt, (b) 3:1 Pt:Pd, (c) 1:1 Pt:Pd, (d) 1:3 Pt:Pd and (e) monometallic Pd catalysts under full mixture conditions. Feed: 5500 ppm CO, 150 ppm C<sub>2</sub>H<sub>4</sub>, 150 ppm C<sub>2</sub>H<sub>6</sub>, 260 ppm C<sub>6</sub>H<sub>14</sub>, 50 ppm C<sub>7</sub>H<sub>8</sub>, 30 ppm NO, 10% O<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O and N<sub>2</sub> balance at a space velocity of 50,000 h<sup>-1</sup>.

In the oxidation of C<sub>7</sub>H<sub>8</sub>, a non-monotonic trend in performance as a function of Pt:Pd ratio was observed (Fig. 1e), with the 1:1 sample showing the best performance. This oxidation behavior is likely due to toluene's unique structure, consisting of benzene ring with  $\pi$ -bonds and the methyl functional group. One possible explanation

is that Pt attacks one type of site and Pd the other. But, the role of the two metals in the bimetallic Pt-Pd samples is not clear, and there is further complicating evidence that reaction mechanisms differ (Eley Rideal vs Langmuir Hinshelwood vs Mars van Krevelen) depending on the metal and support [30–32].

### 3.2. Full mixture feed conditions

The full mixture or complex conditions refer to the experiments where all reactants were co-fed. The CO, NO and hydrocarbon conversions observed over the different catalysts when feeding all the components together are shown in Fig. 3. In all cases, CO oxidation was observed first. Over the monometallic Pt (Fig. 3a), the order in observed conversion was  $\text{CO} > \text{C}_2\text{H}_4 > \text{C}_7\text{H}_8 > \text{C}_6\text{H}_{14} > \text{C}_2\text{H}_6$ . Similar findings, CO oxidizing prior to the hydrocarbon species, have been observed previously [4,5,12,33,34]. This is attributed to the strong adsorption of CO, and once its oxidation begins, sites become available for adsorption and onset of oxidation of the other species. The  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  light off at about the same temperature, and  $\text{C}_2\text{H}_4$  achieved higher conversions more rapidly.  $\text{C}_6\text{H}_{14}$  on the other hand lit off just after the other two hydrocarbons and its conversion reached a relative maximum of  $\sim 80\%$ . This plateau, as discussed above, is attributed to formation of surface intermediates. No  $\text{C}_2\text{H}_6$  conversion was observed.

In terms of NO oxidation, only 13% NO conversion was achieved by  $350^\circ\text{C}$  and negligible conversion was noted until most of the hexane was oxidized. Previous research has shown that  $\text{NO}_2$  is a strong CO and hydrocarbon oxidant over Pt-based catalysts and any formed is reduced back to NO. Thus a lack of conversion is often observed until near complete CO and hydrocarbon removal [36,37].

In comparing the monometallic Pt with the 3:1, 1:1 and 1:3 Pt:Pd catalysts (Fig. 3b–d), the species oxidation order was similar, except with the addition of Pd  $\text{C}_7\text{H}_8$  oxidized before  $\text{C}_2\text{H}_4$ . Moreover, the overall oxidation performance was improved with the addition of Pd. For example, CO oxidation over the 1:1 Pt:Pd sample was observed at  $\sim 140^\circ\text{C}$  and 90% conversion ( $T_{90}$ ) was achieved at  $188^\circ\text{C}$ , while with the Pt-only, 90% conversion was attained at  $297^\circ\text{C}$  and conversion was first observed at  $\sim 200^\circ\text{C}$ . Moreover, the addition of Pd resulted in hydrocarbon oxidation at lower temperature, particularly in the case of  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  species. For the bimetallic catalysts, although hexane oxidation lit off at a lower temperature, its rate of conversion change with temperature was slower compared to the monometallic Pt catalyst. It also worth noting that the bimetallic samples were able to achieve  $>80\%$  conversion indicating that the intermediate species over the bimetallic catalysts resulted in less inhibition compared to the Pt-only sample.

As shown in Fig. 3e, the monometallic Pd catalyst resulted in the best CO oxidation performance, and  $\text{C}_2\text{H}_6$  oxidation improved with increasing Pd content. The onset of  $\text{C}_7\text{H}_8$  oxidation followed that of CO, but not as immediately as with the Pt-containing samples. This was similarly observed in the case of  $\text{C}_2\text{H}_4$  oxidation, where the increase in difference required for CO and  $\text{C}_2\text{H}_4$  oxidation light off temperatures increased as a function of Pd content. This increase or apparent delay in oxidation is due to the lower temperature required for CO oxidation with increasing Pd content. Since CO adsorption is inhibiting the oxidation of the other species, as the temperature for the onset of CO oxidation decreases, the inhibition effect is shifted to lower and lower temperatures and at some point it will be lower than that required for the onset of the hydrocarbon species oxidation in the absence of such an inhibitor. For example, the results shown in Fig. 1 demonstrate that the onset of  $\text{C}_7\text{H}_8$  oxidation in the absence of CO, and other hydrocarbons, is  $\sim 150^\circ\text{C}$ , which is similar to the light off temperature over the monometallic Pd catalyst under the full mixture test conditions.

The  $T_{90}$  values, as another way to compare, for CO,  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  oxidation are plotted as a function of Pt:Pd ratio in Fig. 4. CO poisoning dominates the performance as the hydrocarbon oxidation light off temperatures consistently followed that of CO, regardless of the Pt and Pd content. In the case of CO oxidation, a drastic  $T_{90}$  decrease, from 295 to  $188^\circ\text{C}$ , was observed with the addition of Pd up to 1:1 Pt:Pd, while a further increase in the Pd

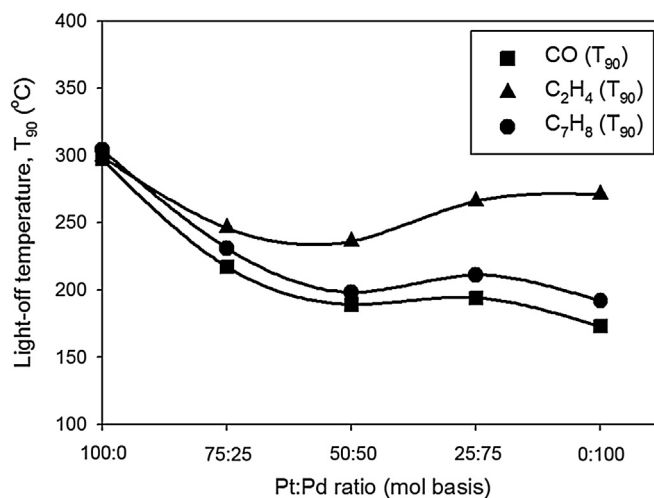


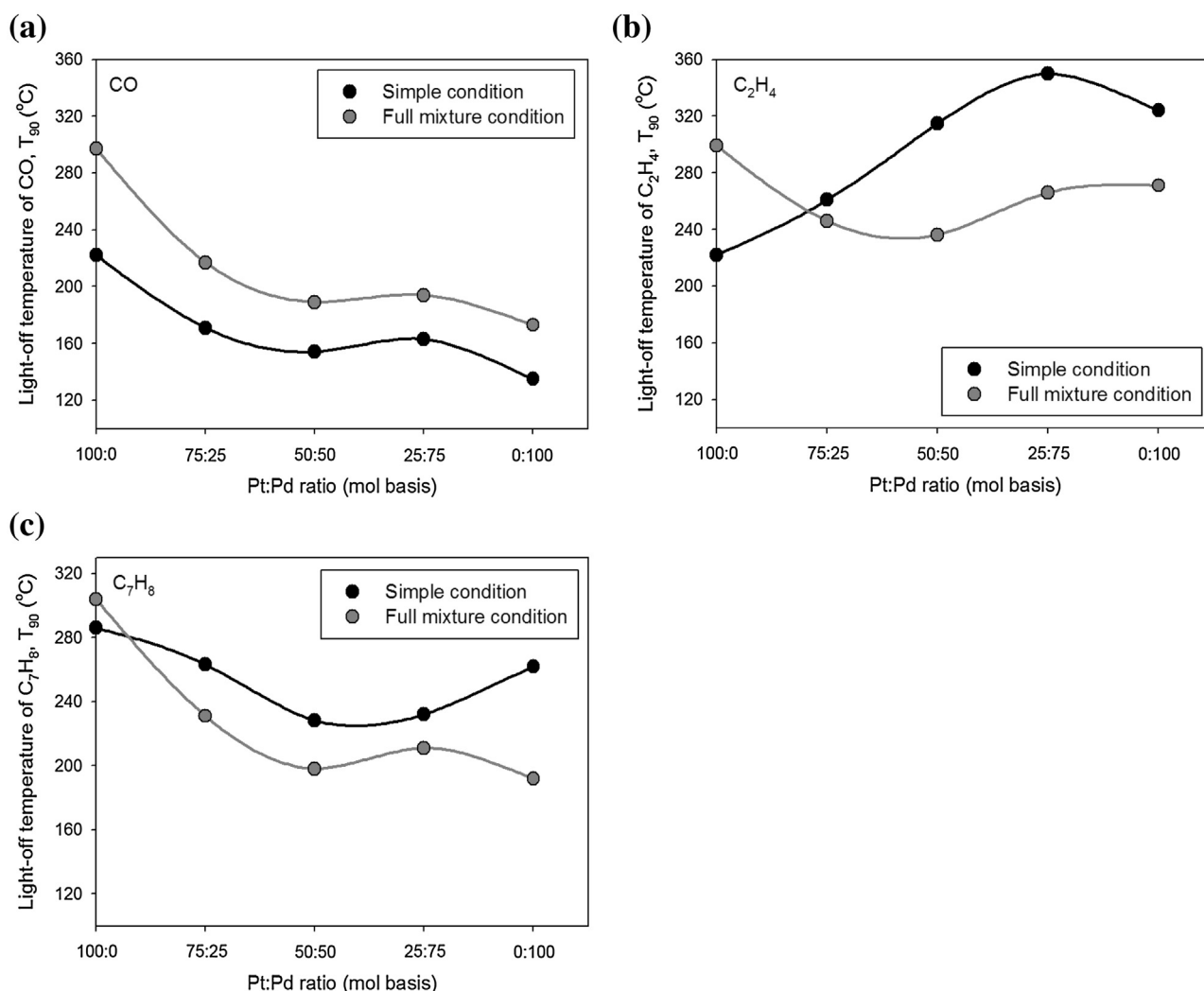
Fig. 4. Light-off temperatures as  $T_{90}$  values for CO,  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  oxidation as a function of Pt:Pd mole ratio under full mixture conditions. Feed: 5500 ppm CO, 150 ppm  $\text{C}_2\text{H}_4$ , 150 ppm  $\text{C}_2\text{H}_6$ , 260 ppm  $\text{C}_6\text{H}_{14}$ , 50 ppm  $\text{C}_7\text{H}_8$ , 30 ppm NO, 10%  $\text{O}_2$ , 5%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$  and  $\text{N}_2$  balance at a space velocity of  $50,000\text{ h}^{-1}$ .

content still led to some decrease in  $T_{90}$  temperature but to a lesser extent. Similarly, higher Pd content initially led to improved  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  oxidation activity, although previous studies have reported that Pt was more effective for hydrocarbon oxidation in comparison of Pd, except for short chain alkane species such as methane and ethane [23,38]. This apparent improved performance in  $\text{C}_2\text{H}_4$  and  $\text{C}_7\text{H}_8$  oxidation is due to the coincident decreased CO oxidation light off temperature, and thus decreased temperature where inhibition plays a significant role. However, for higher Pd content, i.e. 1:3 Pt:Pd and monometallic Pd samples, the  $\text{C}_2\text{H}_4$  oxidation performance decreased. Again, this latter trend is consistent with Pt being more active in olefin and paraffin oxidation than Pd [5,11,12] and is observed due to the decreased impact of CO poisoning. Thus, overall,  $\text{C}_2\text{H}_4$  oxidation is mainly controlled by CO poisoning for high Pt content samples [5,33], but as the light off for CO oxidation dropped with the addition of relatively more Pd, the influence of the precious metal's inherent activity in  $\text{C}_2\text{H}_4$  oxidation was ultimately observed.

### 3.3. Simple vs. full mixture feed conditions

In comparing the two types of experiments, there are some obvious differences in trends, but also clear consistencies. In terms of  $\text{C}_2\text{H}_6$ , in both cases, i.e. in the experiment with just  $\text{C}_2\text{H}_6$  as the hydrocarbon reactant and in the experiment with all the hydrocarbons and CO included, with increased Pd content, although the conversions were low, better performance was achieved. This was expected, as Pd is known to be the better  $\text{CH}_4$  oxidation catalyst as well. Hexane, a longer chain alkane, followed a different pattern. The monometallic Pt sample proved best, with this alkane oxidation difference discussed above in terms of the two metals having different efficacies in cleaving C–C versus C–H bonds. In both experiment types, the same  $\text{C}_6\text{H}_{14}$  oxidation pattern as a function of Pt:Pd ratio was observed; more Pt, better oxidation conversion. CO oxidation was also consistent between the two experiment types, as shown in Fig. 5a, where the  $T_{90}$  values are plotted as a function of Pt:Pd ratio. Higher Pd content led to better CO oxidation in both the simple and full mixture feed conditions.

On the other hand, ethylene and toluene oxidation trends were not consistent between the two feeds (Fig. 5b and c). In the simple feed case, the higher Pt content results in better  $\text{C}_2\text{H}_4$  oxidation performance, with the monometallic Pt catalyst the most active sample. On the contrary for the case of the full mixture feed, the



**Fig. 5.**  $T_{90}$  values for (a) CO, (b)  $C_2H_4$  and (c)  $C_7H_8$  oxidation as a function of Pt:Pd ratio obtained with the simpler feed and full mixture conditions. Simpler feed: 5500 ppm CO or 150 ppm  $C_2H_4$  or 230 ppm  $C_7H_8$ , 10%  $O_2$ , 5%  $CO_2$ , 5%  $H_2O$  and  $N_2$  balance. Full mixture feed: 5500 ppm CO, 150 ppm  $C_2H_4$ , 150 ppm  $C_2H_6$ , 260 ppm  $C_6H_{14}$ , 50 ppm  $C_7H_8$ , 30 ppm NO, 10%  $O_2$ , 5%  $CO_2$ , 5%  $H_2O$  and  $N_2$  balance at a space velocity of  $50,000\ h^{-1}$ .

best sample proved to be the 1:1 Pt:Pd, with monometallic actually Pt proving to be the worst. For the higher Pt content samples the pattern follows CO oxidation, whereas at higher Pd content it follows the simple feed condition pattern. This combined pattern is dictated by CO inhibition. Pt is more susceptible to CO poisoning but more active toward  $C_2H_4$  oxidation. Thus, at high Pt loads, the poor  $C_2H_4$  oxidation performance is due to strong CO poisoning. Nonetheless, at lower Pt content the poor performance is due to the relatively lower activity associated with Pd toward  $C_2H_4$  oxidation. Similarly, in the case of toluene under the simple feed condition, the minimum in light off was observed 1:1 Pt:Pd sample, but with the full mixture feed, the  $C_7H_8$  oxidation followed the CO oxidation pattern, made a bit more apparent in comparing the data shown in Fig. 4. Overall, the oxidation of species with lower oxidation light off temperatures was a function of both CO oxidation light off and Pt:Pd ratio, while those with higher oxidation light off temperatures were a function of Pt:Pd ratio only since CO oxidation occurred at much lower relative temperatures and its inhibition was therefore not pronounced.

Besides the CO inhibition effect, another key factor influencing oxidation trends can be the exotherm generated when the CO and hydrocarbon species are oxidized. As an example, in evaluating CO

and  $C_2H_4$  oxidation over the 1:1 Pt:Pd sample results, plotted in Fig. 6a, CO oxidation was inhibited by the presence of the other hydrocarbon species. The onset of  $C_2H_4$  oxidation was also shifted to higher temperatures demonstrating inhibition by CO. However, once light off was achieved, higher  $C_2H_4$  conversions were attained at much lower temperatures in the presence of CO versus in its absence. This is due to the heat generated via CO oxidation. The adiabatic temperature rise for oxidation of 5500 ppm CO is  $\sim 50^\circ C$ , which is more than sufficient to induce the rapid conversion rate of change with temperature when compared to the absence of CO, or other hydrocarbons. Similar findings were also observed with the other samples, with the monometallic Pd sample as a further examples illustrated in Fig. 6b.

Summarizing, in the present study strong CO inhibition of hydrocarbon oxidation was observed, as has been well-reported in literature [4,5,34,35,39]. Moreover, hydrocarbon inhibition of CO oxidation was observed, as has also been previously reported [6,12,33,40,41]. Using these data, a model has been developed that describes these mutual inhibitions and light off behavior as a function of the Pt:Pd ratio [42]. It is apparent that the most important performance indicator amongst the studied samples and feed conditions is CO oxidation. The lower the CO oxidation light off

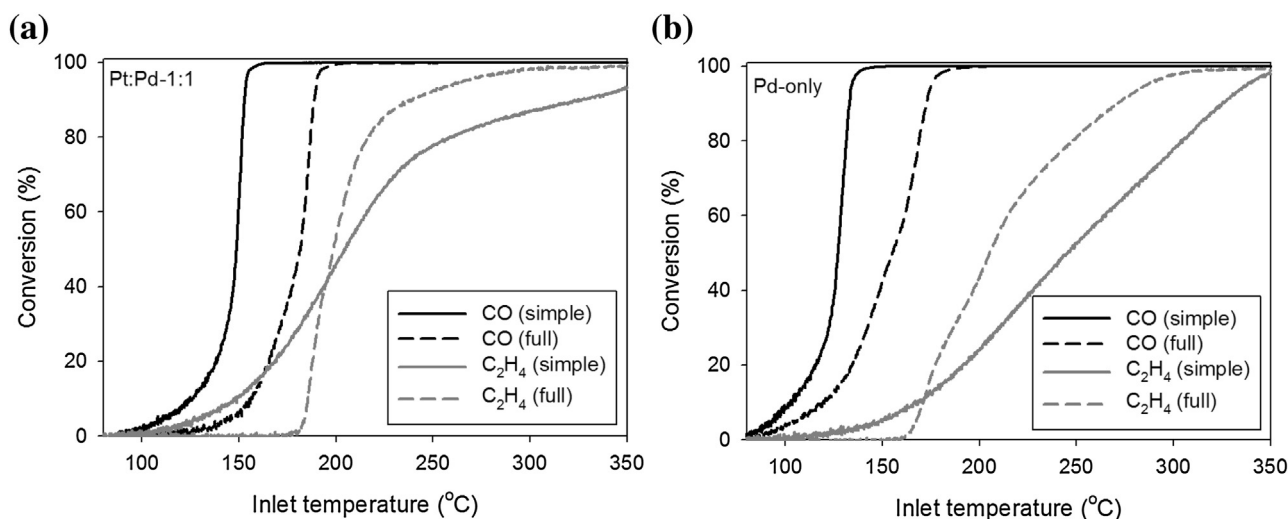


Fig. 6. CO and C<sub>2</sub>H<sub>4</sub> conversions over the (a) 1:1 Pt:Pd and (b) monometallic Pd catalysts under simple and full mixture conditions.

temperature, the better alkene oxidation performance. Hexane and ethane oxidation were less impacted by CO inhibition as their light off temperatures were higher than that of CO for all samples examined.

#### 4. Conclusions

The effect of Pt:Pd ratio on CO and hydrocarbon oxidation was investigated under two sets of reactor inlet conditions. In the case of the simple feed condition, containing only CO or a single hydrocarbon, oxidation activities for CO and C<sub>2</sub>H<sub>6</sub> increased with increasing Pd content in the catalyst. The opposite was observed for C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>14</sub> oxidation where higher reactivity was observed with the monometallic Pt catalyst. With the full mixture feed, hydrocarbon oxidation was not observed until after CO oxidation light off, regardless of the Pt:Pd formulation, demonstrating strong CO poisoning of the catalyst surface. On the other hand, after the light off temperature is achieved, the presence of CO in the feed stream can promote oxidation activity via the exotherm generated from its oxidation. For the bimetallic catalysts, C<sub>2</sub>H<sub>4</sub> and C<sub>7</sub>H<sub>8</sub> oxidation were both influenced by both CO inhibition and the inherent activity of Pt vs Pd. At higher Pd content, less CO poisoning was noted, and at higher Pt content better alkene oxidation was noted. The results of the present work demonstrate that CO oxidation is a critical factor in comparing catalysts for aftertreatment applications. In addition, it is suggested that the use of a single hydrocarbon feed is inappropriate to probe the oxidation kinetics under realistic conditions where other species are present.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.05.057>.

#### References

- [1] U. Asad, R. Kumar, M. Zheng, J. Tjong, *Appl. Energy* 157 (2015) 838–850.
- [2] M. Zheng, U. Asad, G.T. Reader, Y. Tan, M. Wang, *Int. J. Energy Res.* 33 (2009) 8–28.
- [3] D. Han, A.M. Ickes, S.V. Bohac, Z. Huang, D.N. Assanis, *Fuel* 99 (2012) 13–19.
- [4] M.J. Hazlett, W.S. Epling, *Catal. Today* 267 (2016) 157–166.
- [5] M.J. Patterson, D.E. Angove, N.W. Cant, *Appl. Catal. B: Environ.* 26 (2000) 47–57.
- [6] S.B. Kang, S.B. Nam, B.K. Cho, I.-S. Nam, C.H. Kim, S.H. Oh, *Catal. Today* 231 (2014) 3–14.
- [7] A. Morlang, U. Neuhausen, K.V. Klementiev, F.-W. Schütze, G. Miehe, H. Fuess, E.S. Lox, *Appl. Catal. B: Environ.* 60 (2005) 191–199.
- [8] M. Kaneeda, H. Iizuka, T. Hiratsuka, N. Shinotsuka, M. Arai, *Appl. Catal. B: Environ.* 90 (2009) 564–569.
- [9] M.V. Twigg, *Catal. Today* 163 (2011) 33–41.
- [10] A.P. Russell, W.S. Epling, *Catal. Rev. Sci. Eng.* 53 (2011) 337–423.
- [11] M. Skoglundh, L.O. Löwendahl, J.-E. Ottersted, *Appl. Catal.* 77 (1991) 9–20.
- [12] C.H. Kim, M. Schmid, S.J. Schmieg, J. Tan, W. Li, *SAE Tech. Pap. No.* 2011-01-1134, 2011.
- [13] J.E. Etheridge, T.C. Watling, A.J. Izzard, M.A.J. Paterson, *SAE Tech. Pap. No.* 2015-01-1053, 2015.
- [14] B.M. Shakyia, B. Sukumar, Y.M. López-De-Jesús, P. Markatou, *SAE Tech. Pap. No.* 2015-01-1052, 2015.
- [15] S.B. Kang, H.J. Kwon, I.-S. Nam, Y.I. Song, S.H. Oh, *Ind. Eng. Chem. Res.* 50 (2011) 5499–5509.
- [16] D. Roth, P. Gélin, A. Kaddouri, E. Garbowski, M. Primet, E. Tena, *Catal. Today* 112 (2006) 134–138.
- [17] E.N. Coker, W.A. Steen, J.T. Miller, A.J. Kropf, J.E. Miller, *J. Mater. Chem.* 17 (2007) 3330–3340.
- [18] M.O. Nutt, J.B. Hughes, M.S. Wong, *Environ. Sci. Technol.* 39 (2005) 1346–1353.
- [19] H. Shinjoh, H. Muraki, Y. Fujitani, *Stud. Surf. Sci. Catal.* 71 (1991) 617–628.
- [20] L. Glover, R. Douglas, G. McCullough, M. Keenan, P. Reverault, C. McAtee, *SAE Tech. Pap. No.* 2011-24-0193, 2011.
- [21] S. Salomons, M. Votsmeier, R.E. Hayes, A. Drochner, H. Vogel, J. Gieshof, *Catal. Today* 117 (2006) 491–497.
- [22] R. Chen, Z. Chen, B. Ma, X. Hao, N. Kapur, J. Hyun, K. Cho, B. Shan, *Comp. Theor. Chem.* 987 (2012) 77–83.
- [23] K. Persson, A. Ersson, K. Jansson, J.L.G. Fierro, S.G. Järås, *J. Catal.* 243 (2006) 14–24.
- [24] G.R. Bamwenda, A. Ogata, A. Obuchi, J. Oi, K. Mizuno, J. Skrzypek, *Appl. Catal. B: Environ.* 6 (1995) 311–323.
- [25] P. Gélin, L. Urfels, M. Primet, E. Tena, *Catal. Today* 83 (2003) 45–57.
- [26] P. Gélin, M. Primet, *Appl. Catal. B: Environ.* 39 (2002) 1–37.
- [27] F. Diehl, J. Barbier Jr., D. Duprez, I. Guibard, G. Mabilon, *Appl. Catal. B: Environ.* 95 (2010) 217–227.
- [28] T. Maillet, C. Solleau, J. Barbier Jr., D. Duprez, *Appl. Catal. B: Environ.* 14 (1997) 85–95.
- [29] R. Burch, D.J. Crittle, M.J. Hayes, *Catal. Today* 47 (1999) 229–234.
- [30] S. Ordóñez, L. Bello, H. Sastre, R. Rosal, F.V. Díez, *Appl. Catal. B: Environ.* 38 (2002) 139–149.
- [31] Y.-F.Y. Yao, *J. Catal.* 87 (1984) 152–162.
- [32] N. Burgos, M. Paulis, M.M. Antxustegi, M. Montes, *Appl. Catal. B: Environ.* 38 (2002) 251–258.
- [33] J.R. González-Velasco, J.A. Botas, J.A. González-Marcos, M.A. Gutiérrez-Ortiz, *Appl. Catal. B: Environ.* 12 (1997) 61–79.
- [34] K. Hauff, U. Tuttli, G. Eigenberger, U. Nieken, *Appl. Catal. B: Environ.* 100 (2010) 10–18.



- [35] S.-K. Ihm, Y.-D. Jun, D.-C. Kim, K.-E. Jeong, *Catal. Today* 93–95 (2004) 149–154.
- [36] S.R. Katare, J.E. Patterson, P.M. Laing, SAE Tech. Pap. No. 2007-01-3984, 2007.
- [37] K. Irani, W.S. Epling, R. Blint, *Appl. Catal. B: Environ.* 92 (2009) 422–428.
- [38] W.R. Patterson, C. Kemball, *J. Catal.* 2 (1963) 465–478.
- [39] S.E. Voltz, C.R. Morgan, D. Liederman, S.M. Jacob, *Ind. Eng. Chem. Prod. Res. Dev.* 12 (1973) 294–301.
- [40] R. Caporali, S. Chansai, R. Burch, J.J. Delgado, A. Goguet, C. Hardacre, L. Mantarosie, D. Thompsett, *Appl. Catal. B: Environ.* 147 (2014) 764–769.
- [41] I. Amon-Mézière, F. Castagna, M. Prigent, A. Pentenero, SAE Tech. Pap. No. 950932, 1995.
- [42] K. Daneshvar, R.K. Dadi, D. Luss, V. Balakotaiah, S.B. Kang, C.M. Kalamaras, W.S. Epling, *Chem. Eng. J.* 323 (2017) 347–360.